Final Report

GASIFICATION CHARACTERIZATION OF IONIC LIQUIDS AS PROPELLANTS

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Submitted By:

Chung K. Law
Department of Mechanical and Aerospace Engineering
Princeton University
Princeton, NJ 08544

Phone: 609-258-5178
Fax: 609-258-6233
E-Mail: cklaw@princeton.edu

For Consideration By:

Dr. Michael R. Berman
Air Force Office of Scientific Research

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14. ABSTRACT

The objective of the program was to understand and quantify the gasification and oxidation characteristics of droplets of ionic liquids (ILs) in environments of various temperatures and oxygen concentrations. Using 1-ethyl-3-methylimidazolium dicyanamide as a surrogate IL, extensive experiments were performed on suspended and freely falling droplets, and on relating the droplet combustion behavior to the evolution of its internal temperature. Results show that, because of the extreme low volatility of the IL, surface gasification is minimal while internal heating of the droplet is the dominant mode of heat transfer. Furthermore, substantial liquid-phase pyrolytic reaction is initiated when the droplet is heated to 400 °C. This state of heating and pyrolysis continues, leading to the formation of a solid mass. The presence of gas-phase reaction leads to self-sustained combustion of this mass in a high-oxygen environment until complete burnout, while the combustion cannot be self sustained in a low-oxygen environment. The formation of the solid mass and its slow rate of gasification are believed to be a major problem with the utilization of ionic liquids as propellants.

15. SUBJECT TERMS

Ionic liquids; droplet combustion; liquid pyrolysis; carbonization.

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Background and Objectives

AFOSR is interested in the use of ionic liquids (ILs) as an alternative to hydrazine as a propellant. The interest primarily arises from the concern for the precaution and special procedure required to handle hydrazine because of the toxicity of its vapor and thereby potential health hazard to the workers. Since ILs have minimal vapor pressure, at least for the temperature range over which they are handled, such precautions are minimized. Furthermore, being a single-phase system, the mechanical aspects of handling and storage are also considerably simplified. Finally, because of the large number of chemicals that are ILs, and the substantial variation of their molecular constituents and structures, there exists much potential in increasing their energy content through the attachment of various energetic functional groups.

The PI has been extensively involved in combustion studies of high-energy-density liquid materials. Specific materials investigated include HAN-based liquid gun monopropellants that are of interest to the Army, and organic azides and highly-strained compounds such as benzvalenes and cubanes that are of interest to the Navy. Since the volatilities of these compounds are similar to those of JP fuels, their primary mode of combustion is through spray and droplet gasification and burning. Experimental and modeling studies on droplet burning subsequently showed that some of these fuels possess very unique combustion characteristics:

- They exhibit extremely high burning rates as compared to those of JP fuels.
- These high burning rates are primarily consequences of liquid-phase reactions.
- These reactions can also cause catastrophic shattering (termed microexplosion) and hence fine atomization and wide dispersion of the liquid fuel.
- Increasing pressure from atmospheric can significantly increase the burning rates and the propensity for microexplosion.

These combustion studies were profitably conducted in close consultation and collaboration with synthesis chemists, leading to the identification and synthesis of compounds that have high energy contents, high burning rates, and desirable auxiliary combustion characteristics. Furthermore, through these investigations considerable experience and apparatuses were acquired for combustion studies of energetic liquid materials.

In attempting to speculate the combustion characteristics of ILs based on experience with other liquid propellants, one immediately realizes that the extremely low vapor pressure of the ILs could fundamentally affect the dominant mode of liquid gasification. Specifically, since

conventional jet fuels have high vapor pressures, gasification is effected through droplet vaporization. The temperature of the fuel droplets is quite low, being cooled by vaporization and limited by the boiling point of the fuel. For the ILs, however, the low vapor pressure implies that active droplet vaporization and hence liquid gasification may not be too effective. On the other hand, since the droplets can be heated to much higher temperatures in the absence of active vaporization, liquid-phase reactions can be readily initiated which in turn could lead to internal gasification and consequently microexplosion of the droplets. The occurrence of microexplosion would result in instant dispersion and gasification of the droplet mass, thereby providing an alternate means of gasification in spite of the low vapor pressure of the ILs. Furthermore, it is also not unreasonable to speculate that, with increasing droplet temperature, some degree of vaporization can be effected.

The above considerations highlight the importance of assessing the potential role of liquid-phase reaction and droplet microexplosion in the gasification of ILs. The proposed program has several objectives, namely the determination of liquid-phase decomposition temperature, droplet vaporization and combustion rates, the state of droplet microexplosion, if that occurs, and the droplet composition history leading to microexplosion. The investigation is experimental in nature. Most of the objectives have been met during the program period.

Accomplishments on Experimental Investigations on the Gasification and Combustion of Suspended and Freely Falling Droplet of 1-Ethyl-3-Methylimidazolium Dicyanamide

Upon consultation with Drs. G. L. Vaghjiani and T. Hawkins of the Air Force Research Laboratories, it was decided at the start of the program that the candidate ionic liquid to be used is 1-ethyl-3-methylimidazolium dicyanamide. Preliminary experiments were conducted on the "combustion" characteristics of an IL droplet that was suspended at the end of a quartz fiber and subjected to continuous spark discharge in stagnant room air. The droplet size was about 1000 μm. It was observed that, as long as the spark discharge was applied, some form of gas-phase reaction was possible as evidenced by the presence of gas-phase luminosity, leading to the almost complete gasification of the IL. However, if the discharge was terminated before complete droplet gasification, then burning was terminated as well, leaving behind an unburned "solid" mass. Intermittent ejection of small mass fragments from the droplet during combustion was also observed, indicating the presence of liquid-phase reactions through which gaseous products evolved.

Based on these preliminary observations, extensive investigations were performed through four series of experiments: (1) Additional observations on the spark-ignited or spark-sustained fiber-suspended droplet, but now in environments of enriched oxygen, aiming to explore if self-sustained burning can be achieved with oxygen enrichment. (2) Measurement of the temperature of the suspended droplet by using a thermocouple as the suspension fiber, aiming to determine the droplet temperature history and relating it to the observed combustion images. (3) Determination of the droplet temperature at which some form of internal gasification is initiated, for a free, untethered, droplet. (4) Observation of a stream of freely falling droplets in a hot oxidizing or inert environment, aiming to assess the effects of ambient temperature on ignition, as well as the potential fiber effect in the suspended droplet experiments.

Fiber Suspended Droplet Experiment – Combustion Images

Observations were made of the combustion of a single droplet of the ionic liquid, suspended at the end of a quartz fiber and subjected to either continue or brief spark discharge, in environments of various oxygen concentrations. Figure 1 shows the schematic of the apparatus.

Four series of runs were conducted, with 100, 50, 21, and 0% of oxygen in the environment; images of their burning sequences are shown in Figs. 2 to 5, with individual descriptions.
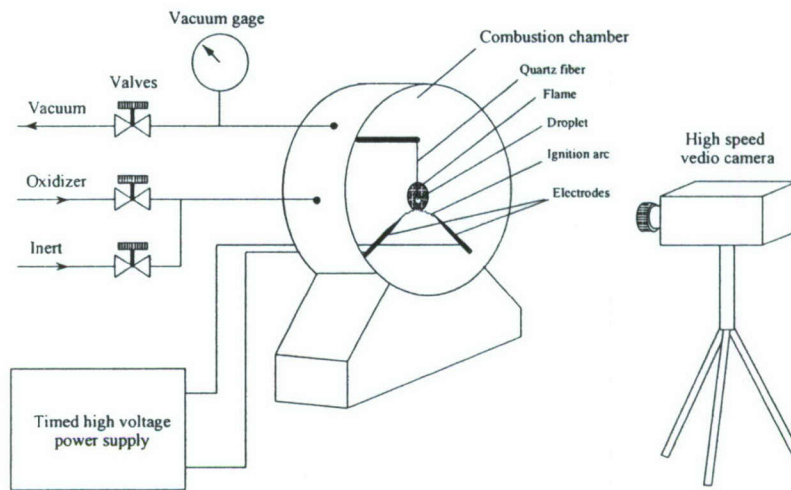
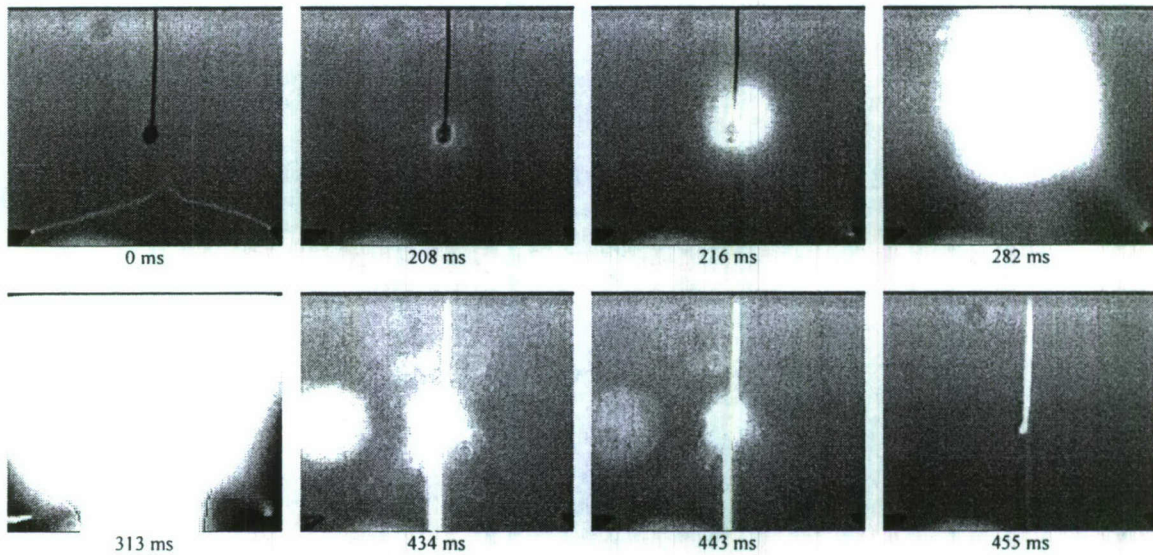Figure 1. Schematic of the suspended droplet apparatus

Figure 2. Burning in 100% oxygen environment

Description: The droplet was preheated during the first 208 ms. Gas-phase "flame" appeared at 210 ms. After discharge was turned off at 434 ms, self-sustained burning continued until the droplet was completely burned out at 455 ms.
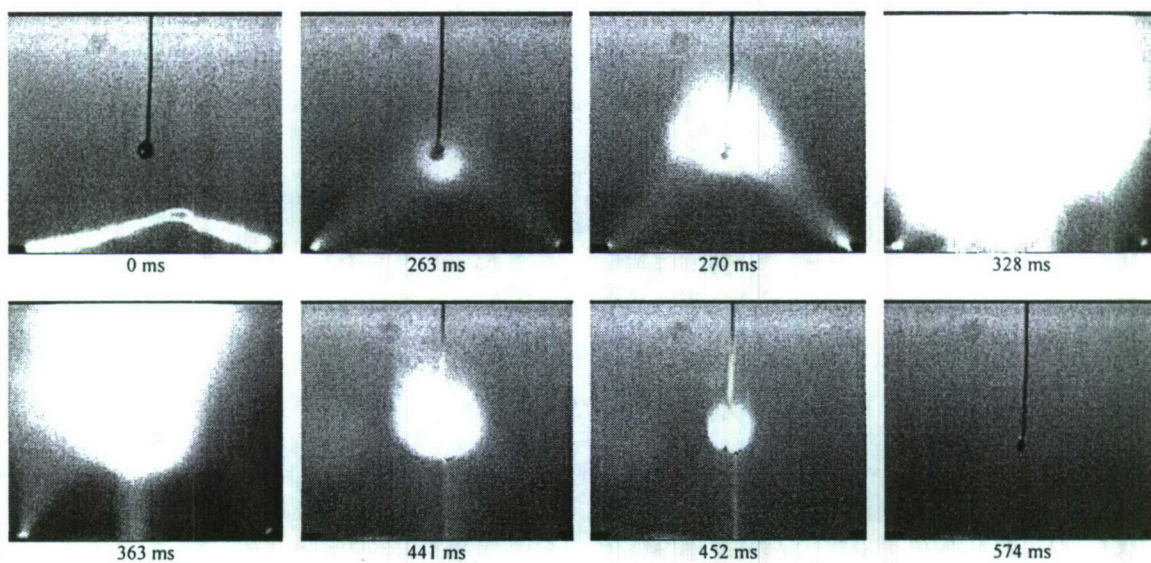
Figure 3. Burning in 50% oxygen environment

Description: The droplet was preheated during the first 263 ms. Gas-phase flame appeared at 263 ms. After the discharge was turned off at 441 ms, self-sustained burning continued until the droplet was completely burned out at 574 ms.
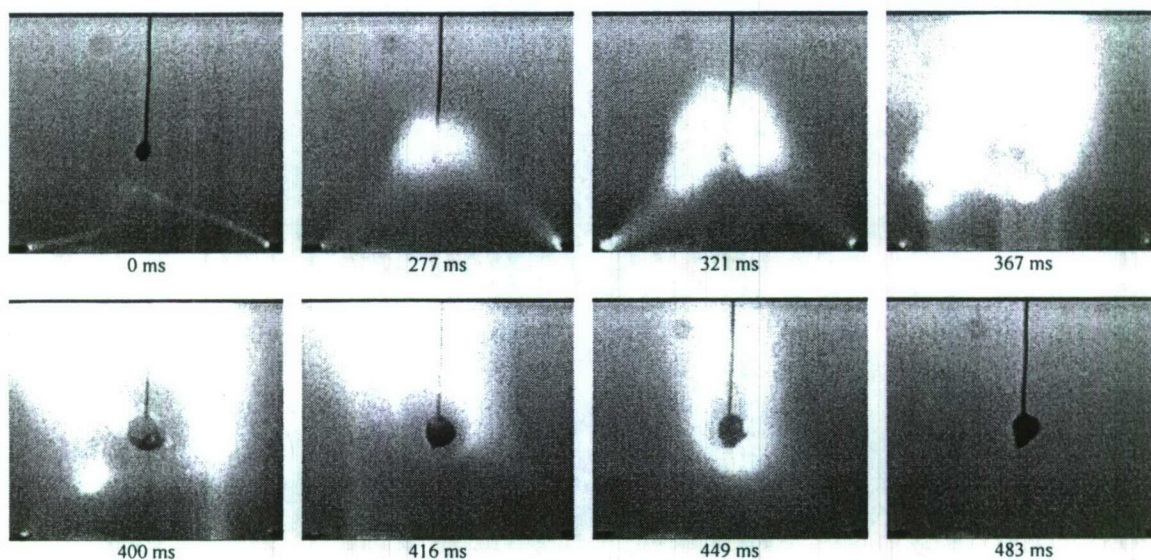

Figure 4. Burning in 21% oxygen environment

Description: The droplet was preheated during the first 277 ms. A solid mass was formed at about 400 ms. After the ignition source was turned off at 449 ms, self-sustained burning could not be maintained, leaving behind the "solid" mass.
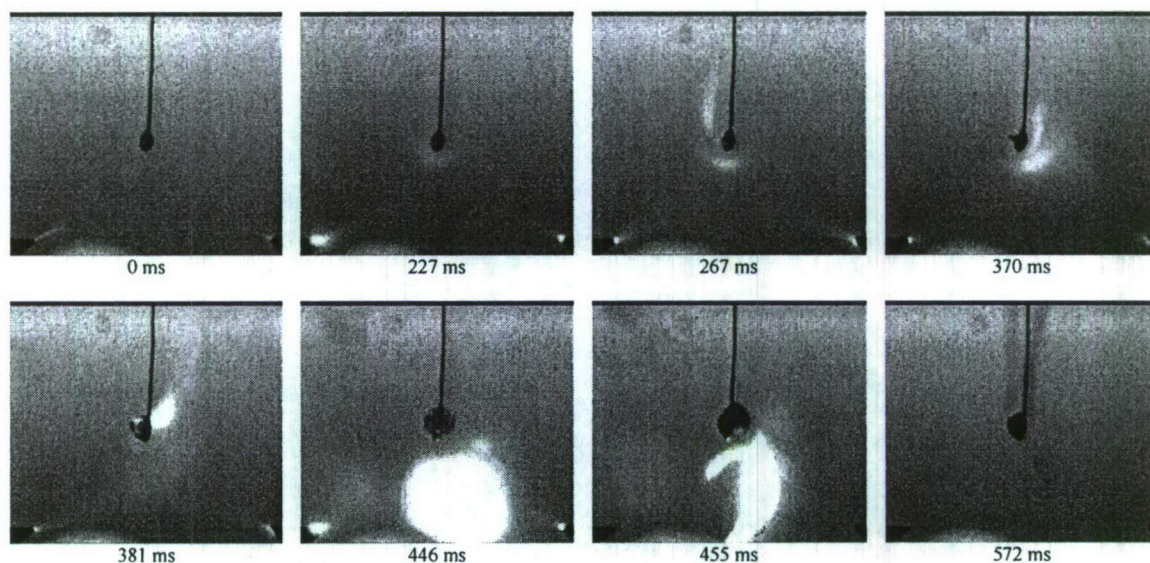
Figure 5. Burning in nitrogen environment

Description: The droplet was preheated during the first 227 ms. From 227 to 455 ms and with discharge turned on, some gas-phase reactions took place as indicated by the gas-phase luminosity. At around 370 ms an irregular solid mass was formed. After the discharge was turned off at 455 ms, the gas-phase luminosity also disappeared, leaving an upward stream of "black" smoke and a black solid mass on the suspension fiber.

Summarizing Description:

Basically, the spark discharge preheats the nominally nonvolatile IL droplet, causing it to swell (to be shown later). Some liquid-phase reaction/decomposition also occurs, causing further swelling and leading to the release of volatiles. This eventually transforms the droplet to a solid mass of irregular shape. The volatiles released undergo some form of gas-phase reaction, which is present even in the inert environment of nitrogen. The gas-phase reaction is much more intense in oxygen-enriched environments. For oxygen volume fraction higher than 50% (although it could be somewhere between 21 and 50%), burning persists upon termination of the discharge, leading to the complete "consumption" of the solid mass. In the air or nitrogen environment, "burning" terminates upon cessation of the discharge, leaving behind a solid mass of irregular shape. Intermittent ejection of small mass fragments also occurs in all cases, forming bright flame-like images around the droplet.

Thermocouple-Suspended Droplet Experiment – Droplet Temperature History

To relate the droplet burning images with the droplet temperature, a K-type thermocouple was used as the suspension fiber to record the droplet temperature history. They are shown in Figs. 6 to 11, and discussed in the following.

In general, results show that some gas-phase flame was initiated upon application of the spark discharge as the droplet temperature reaches ~400 C. Upon "ignition" and continuous application of the discharge, the droplet temperature also continuously increases. When the discharge is subsequently terminated, the droplet temperature continuously increases in the pure oxygen environment (Fig. 6) until complete droplet burnout, reaching a maximum temperature that is greater than 1200 C at burnout. In the air environment (Fig. 8), however, there is a modest temperature increase upon cessation of discharge and the gas-phase flame subsequently extinguishes, leaving an unburned mass. The maximum temperature is 600 C. Figure 7, for the 50% oxygen environment, shows the transition behavior in that, upon termination of the discharge, the droplet temperature briefly reduces before increases again, indicating self-sustained burning, until complete burnout with a maximum temperature of 1050 C.
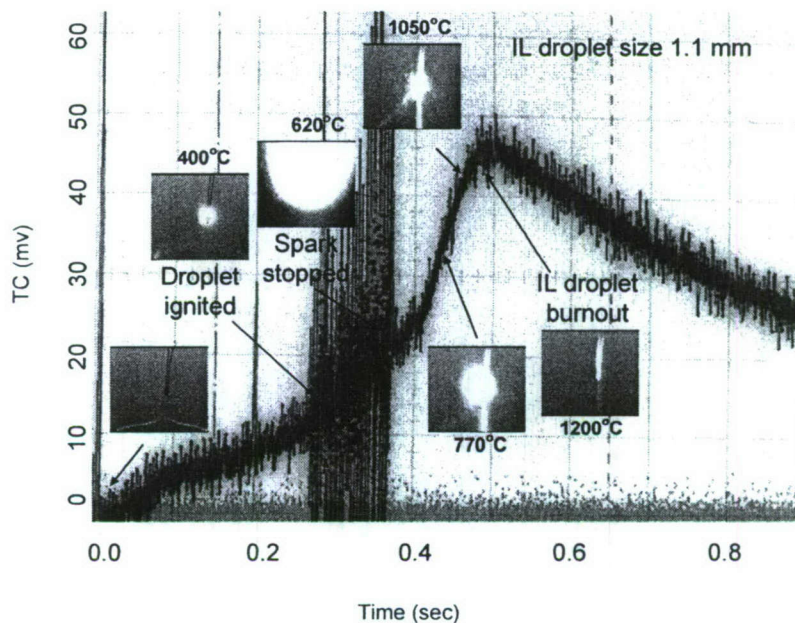

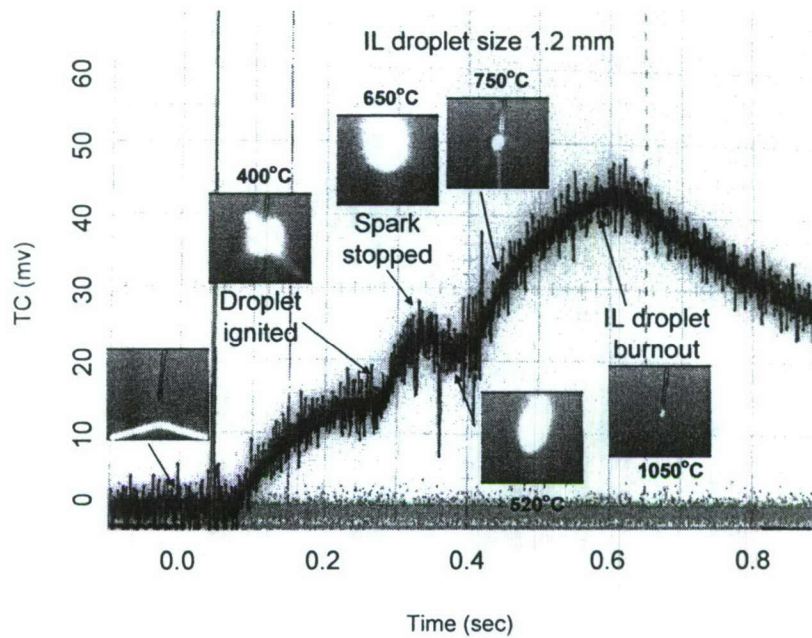Figure 6. Thermocouple record of suspending droplet burning in 100% oxygen environment

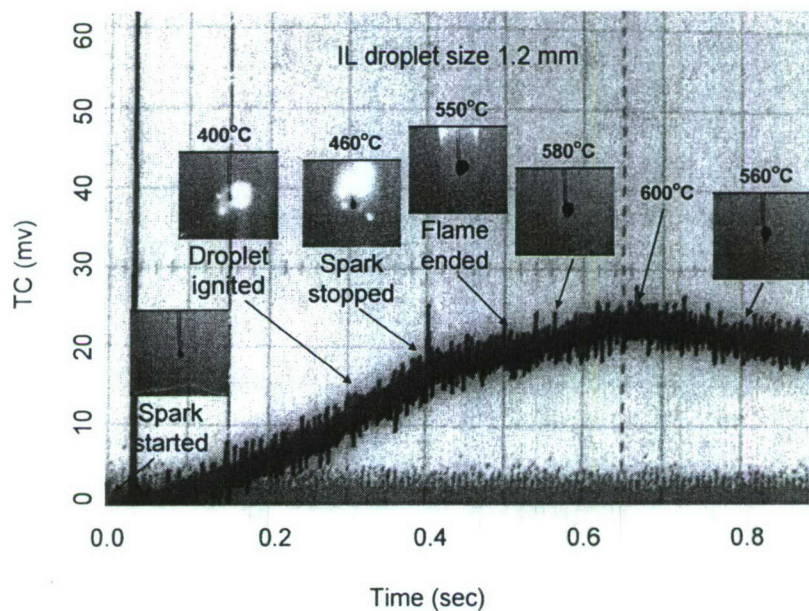Figure 7. Thermocouple record of suspending droplet burning in 50% oxygen environment

Figure 8. Thermocouple record of suspending droplet burning in normal air

To investigate the thermal effect of the spark discharge on burnout in lower oxygen environments, Fig. 9 shows the thermocouple record for burning in air, with continuous discharge. It is seen that the solid mass is continuously heated until it is almost completely "gasified" at about 900 C.
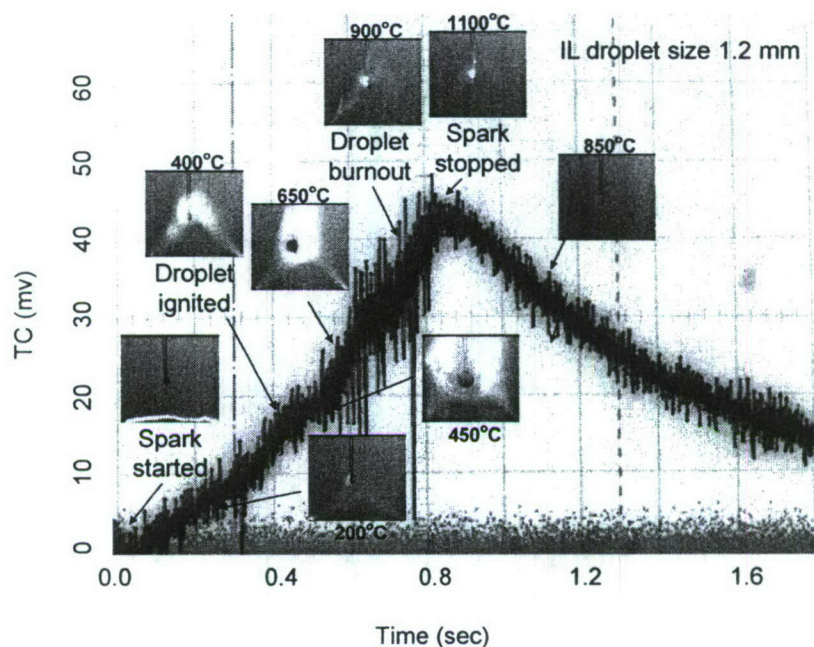
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Figure 9. Thermocouple record of suspending droplet burning in normal air
(with long spark discharge duration)

To assess whether the gasification of the solid mass is aided through oxidation, experiments were performed in the nitrogen environment, with short and long durations of spark discharge, as shown in Figs. 10 and 11, respectively. The results are similar to those in air, indicating that the solid mass can be gasified in the absence of oxygen.
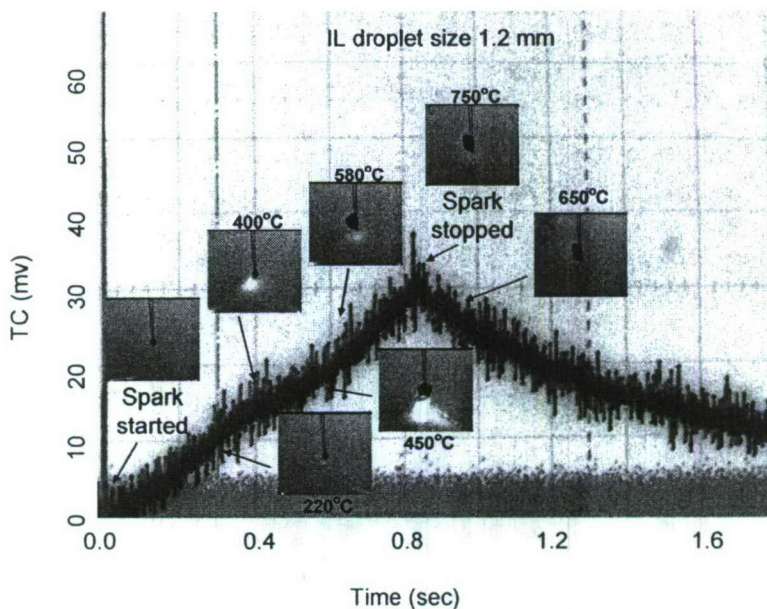

Figure 10. Thermocouple record of suspending droplet burning in nitrogen environment
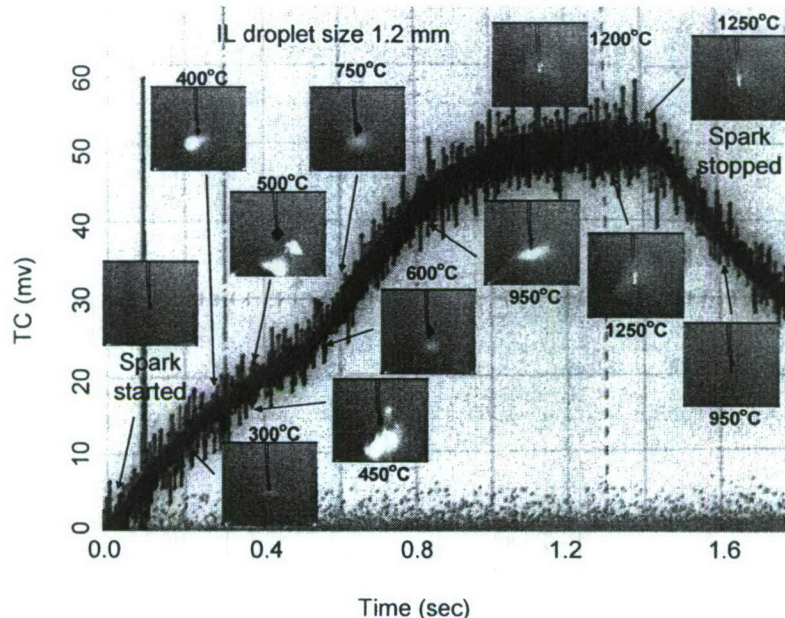(with long spark discharge duration)

Figure 11. Thermocouple record of suspending droplet burning in nitrogen environment (with very long spark discharge duration)

Discussion

These results relate the occurrence of liquid- and gas-phase reactions to the droplet temperature. Volatiles seem to be generated through liquid-phase processes when the droplet temperature reaches 400 C, consequently initiating the gas-phase flame. For enriched oxygen environments, self-sustained burning is possible and is characterized by the continuous increase in the droplet temperature upon cessation of the spark discharge. The question, then, is what is driving this continuous increase. Is it the presence of condensed-phase exothermic reactions, or simply the continuous heating of the droplet by the gas-phase flame? Figure 8 for the air environment shows that there is still a modest temperature increase after the disappearance of the flame, indicating the presence of some condensed-phase reaction. This reaction, however, is not strong enough to sustain the gas-phase flame. On the other hand, the continuous presence of the gas-phase flame and the *substantial* increase of the droplet temperature for the 50 and 100% oxygen environments suggest that it is the gas-phase flame that provides the thermal environment for the gasification.

The continuous increase of the "droplet" temperature to such high values as 1,200 C strongly suggests that the IL has now been "pyrolyzed" to a near-solid mass, which can sustain much higher temperatures than typical liquids whose maximum temperature is limited by its boiling point, which is much lower.

The behavior in air and nitrogen environments is interesting and perplexing. On the one hand, the fact that the solid mass can be eventually gasified again supports the viewpoint that it is the

thermal environment (now provided by the discharge) that sustains the gasification. However, since the gasification is still possible in the non-oxidizing environment, then the gasification is mainly through phase conversion instead of through or being aided by oxidation. Alternatively, some nitrogen chemistry could also facilitate the gasification.

It is of interest to assess the nature of the solid, in particular if it is basically carbon. An independent calculation was then performed for the gasification time of a 1mm carbon particle at 1,200 C in a nitrogen environment. In fact, even without any calculation one could have guessed that carbon would gasify extremely slowly in such a low-temperature, *non-oxidizing* environment, considering that the sublimation temperature of carbon is in excess of 4,000 C. Results show that it would take a couple of years to gasify such a particle! This then suggests that the solid is probably just a low-boiling material such as tar, instead of carbon. In such a case complete gasification within the period of the spark discharge is possible. The presence of nitrogen chemistry could also be facilitating.

Determination of the Explosion Temperature of Freely Rising Droplet

The above results suggest that liquid-phase gasification seems to be initiated around 400 C. There is however some uncertainty of this value as it is conceivable that the reaction or some form of phase change was initiated heterogeneously by the suspension fiber. In order to eliminate this uncertainty, experiments were conducted for an untethered droplet in a constant thermal bath. The experimental apparatus is shown in Fig. 12. Here a column of a high-boiling-point liquid (Krytox 143AD, a fluorinated oil from DuPont. Density: 1.95 g/c.c. at 0 C, 1.78 g/c.c. at 100 C) was electrically heated with a positive upward thermal gradient. A 1mm drop of the IL was introduced at the bottom of the column. It rose slowly due to buoyancy, maintaining perpetual thermal equilibrium with the Krytox bath. The droplet was expected to explode at a distinct location, and hence temperature, if there was internal gas evolution through some physical or chemical phase change processes.

No explosion was observed even when the maximum temperature of the bath was raised to 380 C, at which "smoke" was observed to evolve from its surface, indicating that the thermal limit of the bath liquid was reached. It was not possible to observe any change in color of the droplet as it rose up the column.

A further experiment was conducted by placing a droplet on a thin glass plate, which was slowly heated from the bottom. The plate temperature was measured by a thermocouple. It was observed that the droplet color started to change around 300 C, internal bubbling started at 408 C, and the mass became a black material at 460 C.

The liquid column experiment substantiates the suspended droplet result that phase change in the droplet does not occur before ~400 C. However, it does not rule out the possibility that, in the absence of the suspension fiber, phase change could occur beyond 400 C. We could not locate a host liquid that is thermally stable beyond 400 C.

The heated plate results are in agreement with other results, except that they show that some form of chemical change could take place at 300 C, although without any observable gas evolution.
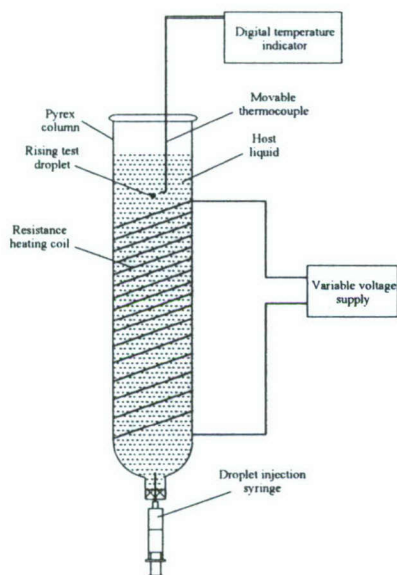

Figure 12. Schematic of freely rising droplet apparatus

Freely Falling Droplet Combustion Experiment

Schematic of the apparatus is shown in Fig. 13. Here a freely falling IL droplet stream was burned in the post-flame environment of a flat methane/air/oxygen (or nitrogen) flame with environments of 21% oxygen, enriched-oxygen (about 30%), or inert (nitrogen/CO_2/H_2O). The droplet stream was produced by a piezoelectric droplet generator of the ink jet type, at 20 Hz. The droplets entered the combustion chamber at its maximum temperature of 1,100 K. These freely falling droplets were substantially smaller than the suspended droplet, around 200 to 300 μm. The limitation here was the insufficient residence time before the droplets exited the burner.

The global flame pictures are shown in Fig. 14 for burning in oxygen-rich and zero oxygen environments, with a bright flame observed for the former and a "dull" flame for the latter.

Because of the limited length of the chamber, the freely falling droplet had only about 100 ms residence time. Consequently droplets with diameters larger than 300 μm could not be ignited. Also, the high-temperature environment of the burner does not permit experimentation with substantially enriched oxygen concentrations. For droplets of 250 μm, ignition could be achieved in the 21% oxygen environment. Figure 15 shows the images of a freely falling droplet in such an environment. The initial diameter of the droplet was 238 μm. The droplet subsequently expanded to about 250 μm before substantial deformation occurred at 28 ms. Gas-phase flame was observed around 50 ms with further deformation and decomposition which released the volatile gas. The flame terminated at 70 ms, leaving a black "solid" material that remained "unchanged" and was collected at the bottom of the combustion chamber.
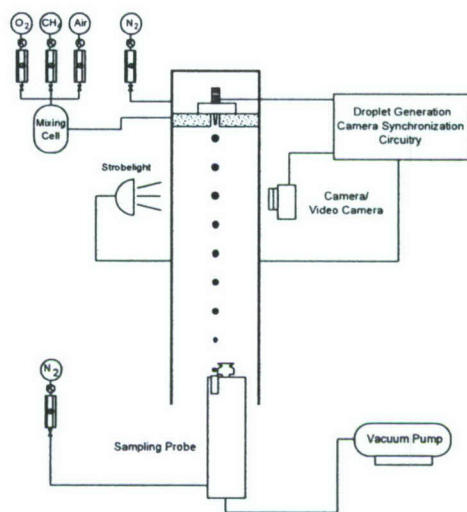
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Figure 13. Schematic of the freely falling droplet apparatus

Flame picture of freely falling IL droplet burning in oxygen rich atmosphere

Flame picture of freely falling IL droplet burning in zero oxygen atmosphere

Figure 14. Global flame images for a stream of freely falling droplets

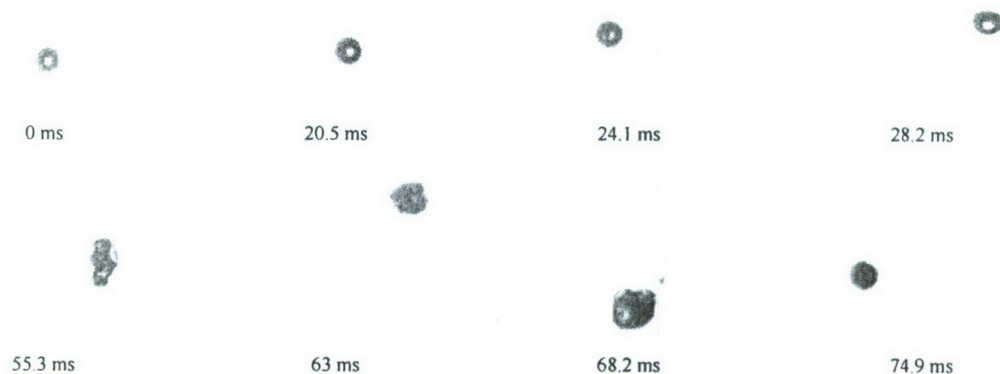| 0 ms | 20.5 ms | 24.1 ms | 28.2 ms |

| 55.3 ms | 63 ms | 68.2 ms | 74.9 ms |

Figure 15. Images of the freely falling droplet

Figures 16a and 16b respectively plot the square of the instantaneous droplet diameter versus time, for the IL droplet and a reference hydrocarbon droplet – dodecane. It is seen that while dodecane follows the classical d^2-law of droplet combustion, the behavior of the IL droplet is totally alien to characteristic droplet burning. As anticipated by now, because of the low vapor pressure and hence higher boiling point of the IL, it initially undergoes substantial heating and hence thermal expansion, trying to reach the (hypothetical) IL boiling point, which could be higher than the decomposition temperature. The high droplet temperature therefore induces liquid-phase pyrolysis, leading to the formation of the irregular-shaped, and possibly porous solid whose gasification process could be fundamentally different from that of the liquid droplet.
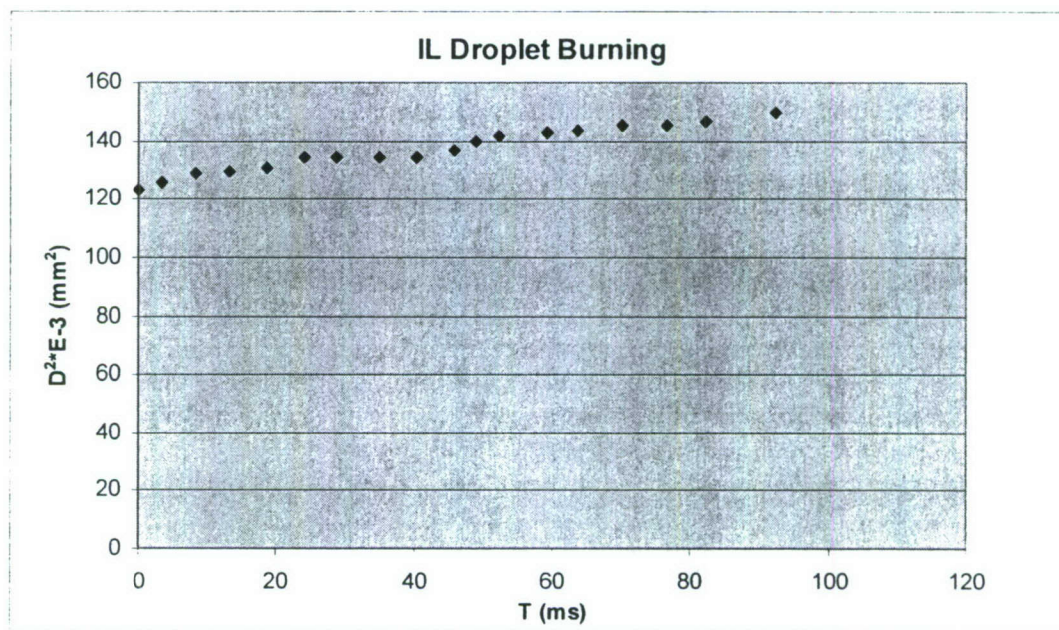

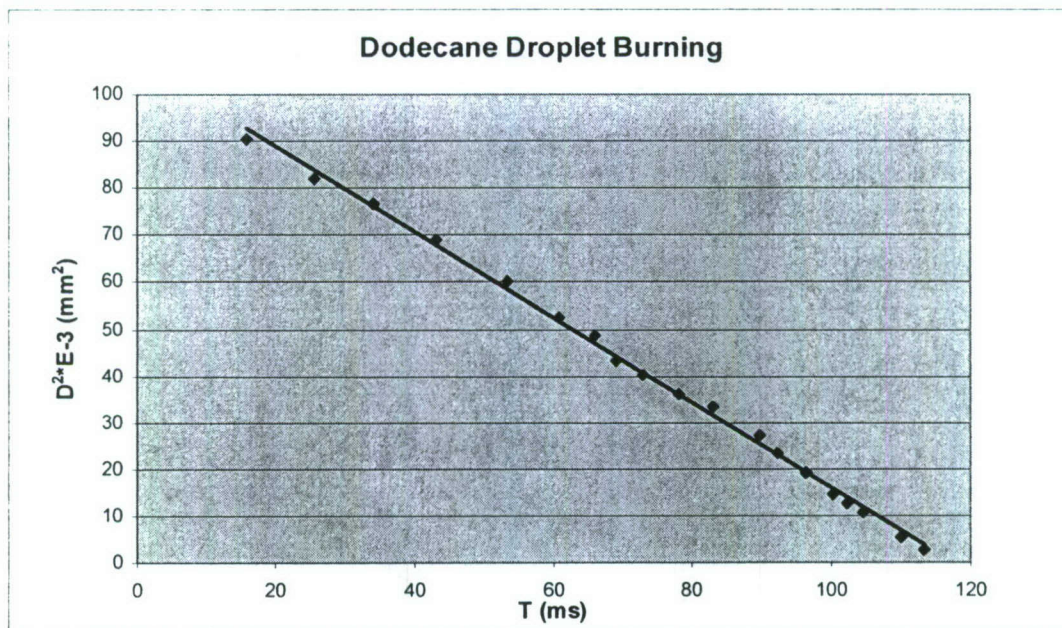Figure 16a. d^2-Law plot of IL droplet burning

Figure 16b. d^2-Law plot of dodecane droplet burning

Figure 17 shows the images of the collected particles. Some of them are black solid pieces while others are thick brown liquids with bubbles inside.
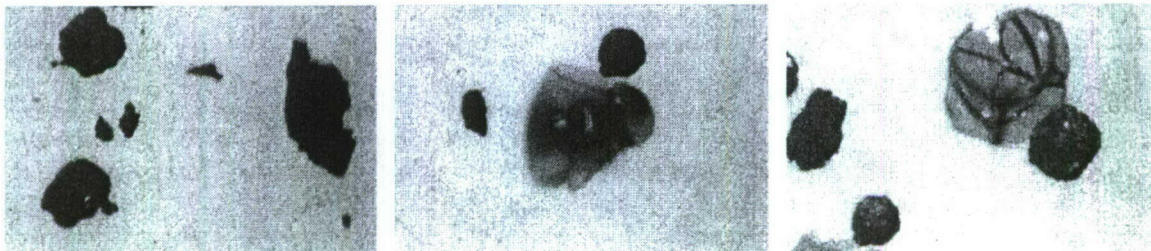

Figure 17. Collected particles from freely falling droplets in 21% O_2

Summary and Concluding Remarks

The observed gasification behaviors of the IL droplet are characteristic of those of very nonvolatile hydrocarbon fuels such as the No. 6 heating oil (if it were pure, without any volatile component). Because of the very low vapor pressure, the droplet will simply be heated up instead of vaporize upon subjected to a thermal environment. This is contrary to the response of conventional volatile fuels such as diesel, kerosene, or JP-8, which would actively gasify when it is heated to a temperature less than 200 C. This active gasification then holds the droplet temperature to a "low" value. For the IL droplet, the minimal vaporization leads to continuous heating of the droplet until pyrolysis is initiated around 400 C. The pyrolysis releases the volatiles that initiate the gas-phase burning.

Upon depletion of the volatiles, the liquid droplet has been pyrolyzed (or mostly carbonized?) to a solid-like material that is expected to be high in carbon content. Because of the extremely low volatility of this material, gas-phase burning cannot be sustained in the normal atmospheric condition. However, in an oxygen-rich or high-temperature environment, continuous burning with the concomitant continuous increase in the particle temperature is possible.

The oxidation and gasification of the pyrolyzed particle in an oxidizing environment can be understood, and its rate predicted, by considering it to be made up mostly of carbon. The gasification in a non-oxidizing environment, however, is perplexing. It is possible that some nitrogen chemistry is involved, with the nitrogen coming from either the original IL, or from the environment.

So what are the practical implications from these results? First, in the normal atmospheric condition, burning of the IL droplet, generated through say spillage, cannot be sustained. This is good because it is for this safety reason that the IL is particularly attractive. It is nevertheless also noted that self-sustained burning is possible in either an enriched oxidizing environment or possibly a high-temperature environment.

Burning rates of these droplets, however, can be very slow especially after it is pyrolyzed. The rates are possibly comparable to those of heating oils that require the long residence times of furnaces and boilers.

So how to facilitate the gasification and burning rates? Hypergolicity is certainly a viable approach, although pyrolysis and solid particles can still be formed. It is however possible that they can be oxidized relatively rapidly.

Another possibility is to emulsify the IL with a small quantity (~1%) of an immiscible liquid that would undergo homogeneous nucleation at a temperature between say 300 to 400 C. Thus when the emulsified IL droplet is heated to this critical temperature, and before it can undergo pyrolysis, the emulsifying liquid would homogeneously nucleate and shatter it to much smaller pieces. This is the concept of micro-explosion. These smaller droplets may still pyrolyze, although the extent could be much smaller because there may not be enough time for the pyrolytic reaction to proceed before these small droplets are gasified.